Reply to Office Action of February 21, 2008

HONG *et al.*
Appl. No. 10/780,863

Remarks

Reconsideration of this Application is respectfully requested.

Claims 1-2, 4, and 6-9 are pending in the application, with claim 1 being the independent claim. Claim 1 has been amended to more fully describe the invention. Support for the amendment to claim 1 can be found in previously presented claims 1 and 3. Claims 3 and 5 have been cancelled. These changes are believed to introduce no new matter, and their entry is respectfully requested.

Based on the following remarks, Applicants respectfully request that the Examiner reconsider all outstanding objections and rejections and that they be withdrawn.

Rejections of claims 1-7 and 9 under 35 U.S.C. § 103(a)

Claims 1-7 and 9 were rejected under 35 U.S.C. §103(a) as allegedly being unpatentable over Hwang *et al.* (*J. Mater. Chem. 11*:1722-1725 (2001)) in view of Smalley et al. (*J. Nanosci. Nanotech 3*:81-86 (2003)). Specifically, the Examiner alleged that Hwang describes a process for forming a carbon nanotube reinforced ceramic nanocomposite by sonication of the CNT solution for 10 minutes. The Examiner acknowledged that Hwang does not provide for an extended sonication period of 2 to 10 hours. The Examiner alleged that Hwang teaches that a stable and homogenous suspension is critical, and that said suspension is achieved through the sonication step. For evidence of this allegation, the Examiner alleged that Smalley describes the relationship between sonication time and CNT dispersion for time periods up to 5 hours. Applicants respectfully traverse this rejection.

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To establish a *prima facie* case of obviousness, the art cited by the Examiner must (1) teach all of the claim limitations; (2) provide a suggestion or motivation to those of ordinary skill in the art to make the claimed composition; and (3) reveal that one of ordinary skill would have a reasonable expectation of success in doing so. *See In re Vaeck*, 20 USPQ2d 1438, 1442 (Fed. Cir. 1991); *see also* M.P.E.P. § 706.02(j). The United States Supreme Court, in *KSR International vs. Teleflex, Inc.*, 550 U.S. ___, WL 1237837 (April 30, 2007), further clarified the requirements for obviousness analysis under 35 U.S.C. § 103(a). The Court noted that the analysis supporting a rejection under 35 U.S.C. § 103(a) should be made *explicit*, and that it was "important to identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the [prior art] elements" in the manner claimed. KSR did not remove the legally established requirement that each element of each claim must be taught in the documents cited by the Examiner.

Claim 1 is the independent claim. Claims 2-7 and 9 are dependent on claim 1.

A.   *A comparison of the present invention to the Hwang disclosure*

Applicants submit that the composite material of Hwang is substantially different than the material of the present invention. Hwang suggests a composite material produced by coating carbon nanotubes with ceramic materials to form <u>nanorods</u>. The nanorods are then combined with ceramic powders, followed by sintering the combined product.

The present invention is directed to providing a method for fabricating ceramic nano composite <u>powders</u> which include a ceramic matrix and carbon nanotubes

homogeneously dispersed in the matrix, thereby preventing agglomeration of the carbon nanotubes.

Applicants submit that Hwang has proposed a technical approach for preparing carbon nanotube composite materials that include nanotubes coated with polymerized ceramic materials. However, as shown in the following FIG. 1, Hwang further requires a process of bulking the precoated polymerized ceramic carbon nanotubes by mixing with general ceramic powders to fabricate ceramic composite materials.

In contrast, the present invention provides nano composite powders, as a principal material that can easily and more conveniently produce nano composite materials in which carbon nanotubes are homogeneously dispersed by sintering, without the additional process of coating the nanotubes with a ceramic material. The present invention is characterized in that nano composite materials, containing carbon nanotubes dispersed therein, are easily obtained by preparing a ceramic matrix of micrometer size in which several to several tens of carbon nanotubes are dispersed to fabricate composite powders and directly sintering the prepared composite powders.

In summary, the present invention directly fabricates nano composite powders in which carbon nanotubes are dispersed by a chemical process to effectively produce nano composite materials containing carbon nanotubes dispersed therein. This process includes the processes of dispersing, mixing, drying, and calciniation, and is summarized in FIG. 1.
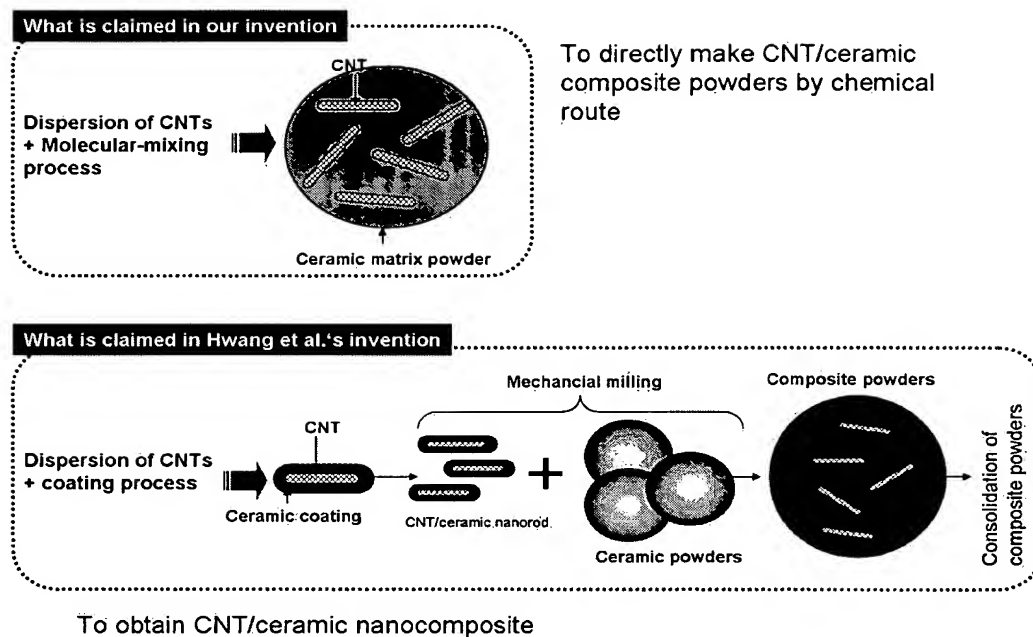
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What is claimed in our invention

Dispersion of CNTs
+ Molecular-mixing
process

CNT

Ceramic matrix powder

To directly make CNT/ceramic
composite powders by chemical
route

What is claimed in Hwang et al.'s invention

Mechancial milling

Composite powders

Dispersion of CNTs
+ coating process

CNT

Ceramic coating

CNT/ceramic nanorod

Ceramic powders

Consolidation of
composite powders

To obtain CNT/ceramic nanocomposite

Figure 1. Diagram illustrating the present invention compared with the cited invention 1.

B.   *Amended claim 1 requires metal-based salts capable of being formed into a ceramic matrix.*

Claim 1 has been amended to require the water-soluble salt to be a metal-based salt capable of being formed into a ceramic matrix. Neither Smalley or Hwang describe the use of metal-based water soluble salts. Thus, each and every element of claim 1 cannot be found in Hwang and Smalley, either individually or collectively. For at least this reason, Applicants respectfully request that the rejection of claims 1-7 and 9 under 35 U.S.C. §103(a) be withdrawn.

C.   *The present invention discloses a ceramic matrix distinct from the polymerized matrix of Hwang*

Hwang discloses the use of polymerized silicate to coat the carbon nanotubes. The silicate polymerization is described in Hwang as follows: "The solution was then slowly titrated (drop by drop) by ~6mL of a 46 mM H_2SO_4 solution to adjust the pH to ~9.5, which initiates polymerization of silicates. *See*, Hwang, pg 1722, 1st col., last ¶ to 2nd col., 1st paragraph.

The present invention discloses a ceramic matrix which is not polymerized. Rather, the present invention teaches the <u>direct contact of CNTs with ions contained in a water-soluble salt. Polymerization does not occur</u>. Instead of polymerization, Applicants claimed invention is a process of gradually converting the water-soluble salt into the ceramic matrix through drying and calcination. The present invention does not utilize pH control, and therefore cannot cause and need not cause polymerization. Consequently, as described in Example 2, a ceramic matrix such as CuO can also be used, even though polymerization is not possible.

Improved characteristics of the nano composite materials sintered from the composite powders of the present invention can be found in *Scripta Materialia 53*:793-797 (2005), which is hereby attached as **Exhibit A**. Fig. 1a of Exhibit A supports the distinction of the present invention, wherein C-Al-O bonding is evidenced by a remarkable bending peak in the FT-IR spectrum of the nanocomposite after completion of drying and calcination processes. In particular, the C-Al-O bonds in the material exhibited a very sharp from 500 to 750 cm^{-1}, that is present only after oxidation is complete.

Further support of the advantages of the present invention can be found in ,

Advanced Materials 17:1377-1381 (2005), which is hereby attached as Exhibit B. This

reference describes a fabrication process of nano composite materials through direct

preparation of nano composite powders.

For at least the above distinctions, Applicants respectfully submit that the

claimed invention is not obvious and request that the rejection of claims 1-7 and 9 under

35 U.S.C. §103(a) be withdrawn.

D.   *Sonication of the present invention promotes chemical bonding between the carbon nanotubes and the ceramic*

One important feature of the presently claimed invention is that bonding between

carbon nanotubes and water-soluble salts is achieved via the sonication process that does

not require the presence of a sufactant. Specifically, the presently claimed invention

allows dispersion of CNTs in any dispersible solvent, even in the absence of a surfactant.

Moreover, the formation of chemical bonds during the sonication, drying and

calcination steps provides CNT composite materials with improved characteristics, due

to the direct bonding of CNTs and water-soluble salts without interference by a

surfactant. Direct bonding is enhanced by the claimed invention in all steps of the

process, e.g., sonication, dispersion, drying, and calcination. Thus, the sequence of the

claimed processes recited in claim 1 achieves an enhanced bonding that is not achievable

by performing any of the claimed steps in isoloation. Each of the claimed processes

have technical efficiencies, each of which is necessary to have an improved and

advanced effect. The present invention is directed to this combination of processes,

which provides for <u>a bonding of CNT and water-soluble salt and, in turn, a strong</u> <u>interface bonding between CNT and ceramic matrix materials</u>.

Hwang does not sonicate for an extended period of time. The Examiner alleged that Smalley teaches an extended sonication time, and teaches the relationship between sonication time and CNT dispersion. However, Hwang and Smalley suggested the use of a surfactant to accomplish optimum dispersion of the carbon nanotubes. In fact, neither document teaches the use of sonication to increase the strong interface chemical bonding of CNT with the ceramic matrix material associated with extended sonication time. That is, both references recite the use of a surfactant on the grounds that the surfactant supports optimum dispersion of carbon nanotubes.

The surfactants used in Hwang and Smalley would form a layer between the carbon nanotubes and the water-soluble salt during sonication. Even during drying and/or calcining, the surfactant would be burnt and form pores between the carbon nanotubes and the ceramic matrix. Hwang recognized this disruption of bonding by devoting many pages in the document to affirm bonding sequence of CNT-surfactant-silicate.

Thus, one of skill in the art trying to fabricate carbon nanotube ceramic powders based on Hwang and/or Smalley would use surfactants to disperse CNT and would not utilize extended sonication times. The present invention overcame the problems in the art by not using surfactants.

For at least the above distinctions, Applicants respectfully submit that the claimed invention is not obvious and request that the rejection of claims 1-7 and 9 under 35 U.S.C. §103(a) be withdrawn.

Rejections of claim 8 under 35 U.S.C. § 103(a)

Claim 8 was rejected under 35 U.S.C. §103(a) as allegedly being unpatentable over Hwang in further view of Chang (U.S. Pat. No. 6,420,293). Specifically, the Examiner alleged that Hwang teaches that the SiO_2-CNT powder is to be calcinated in an N_2 atmosphere at 1050°C, which falls between the claimed temperature range of 400-1700°C. The Examiner acknowledged that Hwang fails to explicitly set forth that the calcination of the ceramic matrix should be performed under a high vacuum. However, the Examiner alleged that Chang teaches that the heating of carbon nanotube materials at elevated temperatures in an oxidizing environment typically results in chemical changes in the surface of the particles, and that both N_2 atmospheres and high vacuum environments are commonly utilized as non-oxidizing environments. Thus, the Examiner alleged that the high vacuum environment would be an obvious alternative to the nitrogen atmosphere in Hwang. Applicants respectfully traverse this rejection.

Applicants submit that the calcination temperature was defined to achieve higher order objectives (or more complicated objectives) in addition to the basic objective such as prevention of CNT damage. That is, calcination under air atmosphere allows combination of CNT such as C-Al-O with the ceramic matrix while supplying sufficient amount of oxygen to a composite of CNT and the water-soluble salt. Calcination under vacuum conditions can efficiently remove hydrated water contained in crystals of the ceramic matrix and accelerate crystallization of the ceramic matrix, leading to easy sintering during further sintering process.

Even other than Chang, persons having ordinary skill in the art can generally determine and/or identify damage of CNT in the air by means of normal measurements including TGA (thermo-gravimetric analysis), and any CNT manufacturers usually offer such data to consumers.

Thus, neither Hwang nor Chang teach or suggest calcination of the ceramic matrix should be performed under a high vacuum as required by claim 1, either individually or collectively. Claim 8 is also dependent on claim 1. Neither Hwang nor Chang describe the ceramic nanocomposite powder as described in the above for claim 1. In view of these arguments, and since Chang does not cure the deficiencies, then each and every element of claim 8 is also not taught or suggested. For at least the above argument, and in further view of the arguments for claim 1-7 and 9 filed herein, the rejection of claim 8 under 35 U.S.C. §103 as allegedly being obvious by Hwang in view of Chang should be withdrawn.

Conclusion

All of the stated grounds of objection and rejection have been properly traversed, accommodated, or rendered moot. Applicants therefore respectfully request that the Examiner reconsider all presently outstanding objections and rejections and that they be withdrawn. Applicants believe that a full and complete reply has been made to the outstanding Office Action and, as such, the present application is in condition for allowance. If the Examiner believes, for any reason, that personal communication will expedite prosecution of this application, the Examiner is invited to telephone the undersigned at the number provided.

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Prompt and favorable consideration of this Reply is respectfully requested.

Respectfully submitted,

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Strengthening and toughening of carbon nanotube reinforced alumina nanocomposite fabricated by molecular level mixing process

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Abstract

A novel process to fabricate carbon nanotube (CNT)/alumina nanocomposites, consisting of a molecular level mixing process and an in situ spark plasma sintering process, is proposed. The CNT/alumina nanocomposites fabricated by this proposed process show enhanced hardness due to a load transfer mechanism of the CNTs and increased fracture toughness arising from the bridging mechanism of CNTs during crack propagation.

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Keywords: Carbon nanotube; Ceramic matrix composite; Molecular level mixing; Spark plasma sintering

1. Introduction

Since the discovery of carbon nanotubes (CNTs), they have been considered as the most promising reinforcements for composite materials to overcome the performance limits of conventional materials [1–3]. Therefore, there have been several attempts to fabricate CNT/alumina nanocomposites with enhanced hardness and toughness [4–8]. However, previously reported CNT/ceramic nanocomposites show much inferior mechanical properties than expected or, in some cases, even worse mechanical properties than those of monolithic ceramic materials [4–7].

Several processes have been proposed to fabricate CNT/ceramic nanocomposites. Zhan et al. fabricated CNT/alumina nanocomposite by blending dispersed single-walled nanotubes with nanocrystalline alumina powders, followed by the spark plasma sintering (SPS) process [4]. The CNT/alumina nanocomposite produced shows much enhanced fracture toughness. However, the hardness of the CNT/alumina nanocomposite decreased with increasing CNT content. CNT/oxide nanocomposites have also been fabricated by growing CNTs on powders mixed with catalyst, followed by the sintering process [5,6]; however, these show little improvement in the fracture toughness.

Such results are far from the properties expected, considering the extraordinary mechanical properties of CNTs. There are two main reasons: one is the weak bonding between CNTs and ceramic matrix and the other is the inhomogeneous distribution of CNTs within the ceramic matrix. Recently, CNTs have been homogeneously dispersed within the alumina matrix by the sol–gel process [8]; however, the interfaces between CNTs and alumina matrix are not strong. The most promising process to obtain homogeneous dispersion of CNTs and strong interfacial strength is the molecular level mixing process, consisting of reaction between functionalized

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CNTs and metal ions in solution, which was originally designed for CNT/metal nanocomposites [9].

In this study, the CNT/amorphous-Al_2O_3 composite powders were fabricated by the molecular level mixing process to obtain strong interfacial bonding and homogeneous mixing between CNTs and Al_2O_3 powders. At the same time, the CNT/amorphous-Al_2O_3 composite powders were consolidated into CNT/alumina nanocomposites by an in situ SPS process.

2. Experimental procedures

2.1. Fabrication of CNT/amorphous-Al_2O_3 composite powders

Multi-walled carbon nanotubes fabricated by chemical vapor deposition were obtained from Iljin Nanotech. Co. The CNTs were acid treated with HF, HNO_3 and H_2SO_4 and oxidized at 190 °C for 4 h to remove catalysis particles and to generate functional groups on the surfaces of the nanotubes; the functionalization of CNT can be obtained by acid treatment as reported elsewhere [10–13]. The acid treated carbon nanotubes were

sonicated for 24 h in distilled water for homogeneous dispersion. $Al(NO_3)_3 \cdot 9H_2O$ was added into a suspension with the carbon nanotubes and these were sonicated for 24 h. This solution was vaporized by heating to 100 °C and the powders that remained were oxidized at 350 °C for 6 h in air atmosphere. The volume fractions of CNTs varied from 0 to 1.8 vol.%. During the calcination process, the chemical bonding between CNT and amorphous Al_2O_3 matrix was formed and confirmed as shown in Fig. 1a.

2.2. Spark plasma sintering

Spark plasma sintering was carried out with Dr. Sinter 1500 SPS machine from Sumitomo Coal Mining Co. The composite powders were compacted in a graphite mould with a diameter of 8 mm and were heated by pulsed electric current at a vacuum pressure of 1 Pa. The heating rate was fixed as 100 °C/min. The hardness of the carbon nanotube reinforced alumina matrix nanocomposite was measured using the Vicker's indentation test under a load of 9.8 N and the fracture toughness was evaluated by measuring the crack length generated after indentation.
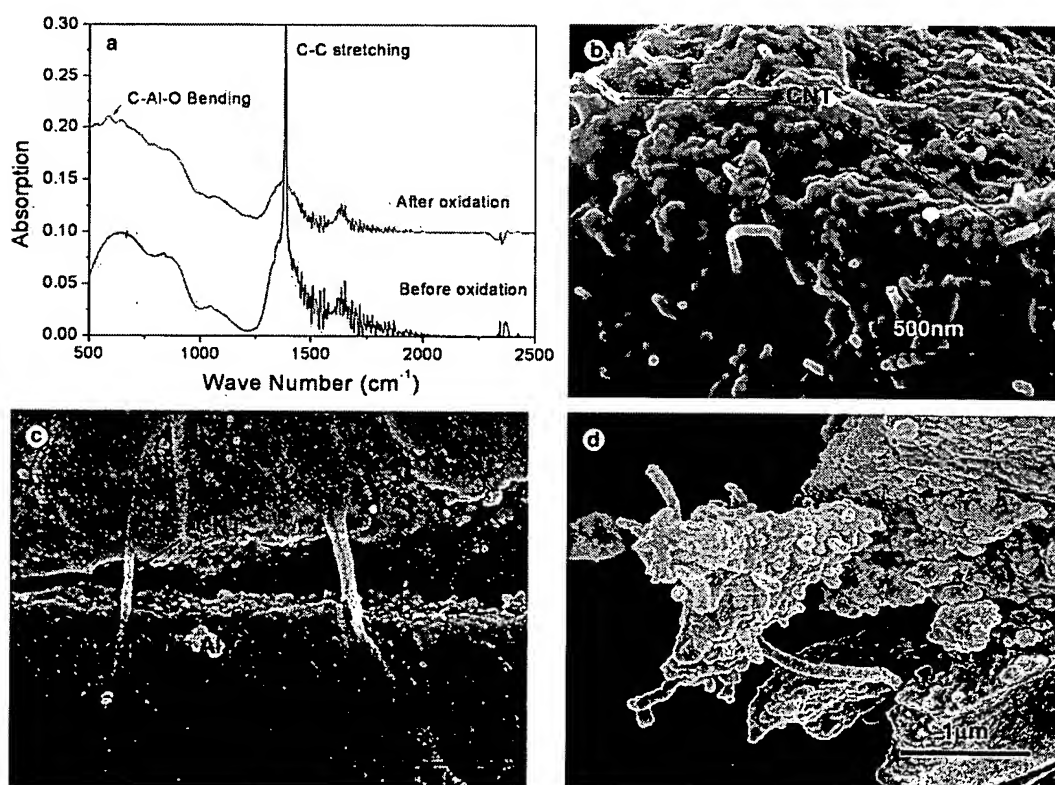

Fig. 1. (a) Fourier transform-infrared analysis of CNT/amorphous-Al_2O_3 composite powders before and after calcination process. (b) SEM micrographs of surface of a CNT/amorphous-Al_2O_3 composite powder, in which carbon tubes were implanted in amorphous-Al_2O_3 powder. (c) Carbon nanotubes showing the bridging mechanism across a crack in amorphous-Al_2O_3 matrix observed from cross-sectional SEM micrographs of CNT/amorphous-Al_2O_3 composite powders. (d) Small amorphous-Al_2O_3 fragment connected to powder by carbon nanotubes.

3. Results and discussion

The above process can produce homogeneously dispersed CNTs implanted in amorphous Al_2O_3 powder with chemical bonding between CNTs and amorphous Al_2O_3. The key feature of this process is that the CNTs and metal ions are mixed homogeneously in an aqueous solution at a molecular level. Therefore, the critical problem of the strong agglomeration of CNTs reported in solid state mixing within a matrix and strong bonding between CNTs and a matrix can be solved by using the molecular level mixing process. The morphology of CNT/Al_2O_3 composite powders showed that the CNTs are homogeneously distributed within the powders as shown in Fig. 1b. In particular, the bridging effect of CNTs across two crack surfaces was observed when the calcinated composite powder was fractured as shown in Fig. 1c.

The composite powders were crystallized and consolidated by the in situ SPS process. SPS enables powder compacts to be sintered by Joule heat and spark plasma generated by pulsed high electric current through the compact [14]. Various information on the crystallization, phase transformation and densification of the CNT/amorphous-Al_2O_3 compact was analyzed from the observation of the shrinkage behavior during the in situ spark plasma sintering. In the first stage, the amorphous-Al_2O_3 powders reinforced with CNTs were crystallized at 600–800 °C and phase transformation occurred at 1000 °C during in situ SPS. In the second stage, the crystallized Al_2O_3 and CNTs were densified into CNT/α-alumina nanocomposite after SPS at 1500 °C for 5 min as shown in Fig. 2a. The XRD analysis indicates that the amorphous Al_2O_3 powders implanted by the CNTs were sintered into CNT/α-alumina nanocomposite by the in situ SPS process as shown in Fig. 2b.

The fracture surface of the sintered CNT/alumina nanocomposite is shown in Fig. 2c. The CNTs were homogeneously dispersed within grains or at grain boundaries of the alumina matrix. It is also shown that the amorphous alumina matrix is completely crystallized into a crystalline α-alumina phase. The most important feature in the fracture surface of the CNT/alumina composites is that the CNTs are pulled-out during the fracture process. In previous reports on CNT/alumina fabricated by conventional mixing of CNT and alumina powders, most of the CNTs were located at grain boundaries of alumina matrix [4]. However, fractography of
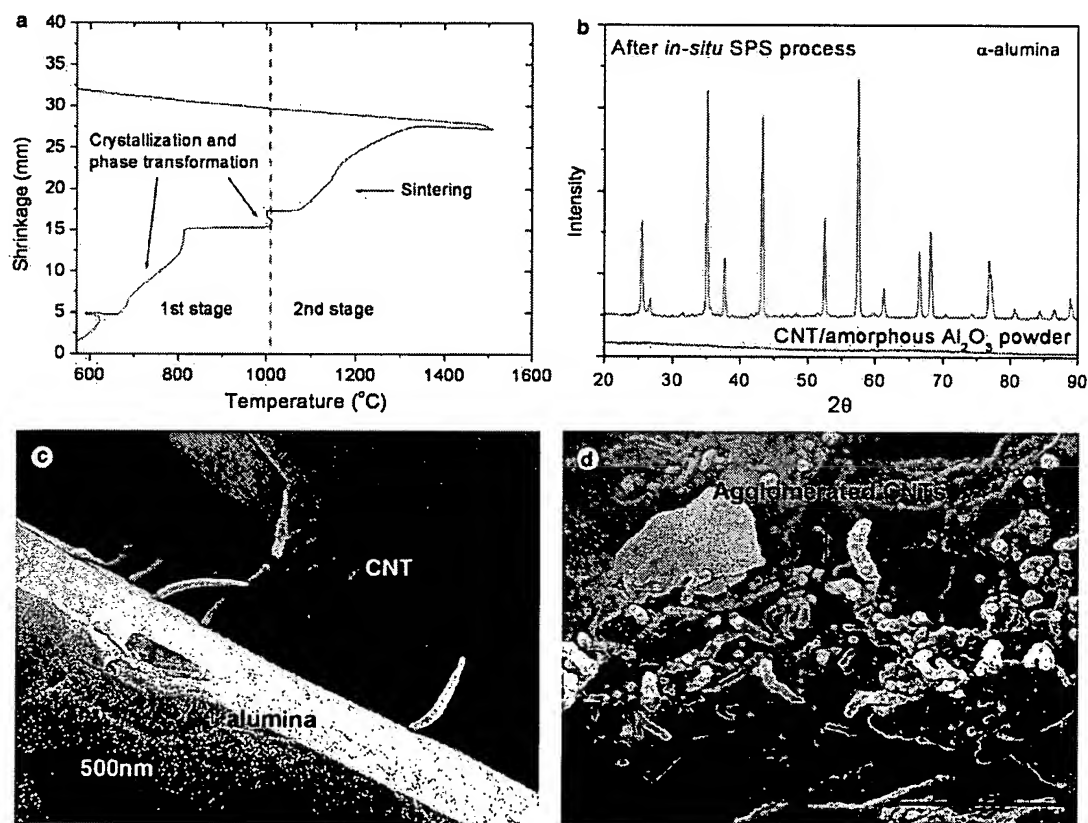

Fig. 2. (a) A plot of shrinkage with increase in temperature during spark plasma sintering of CNT/amorphous-Al_2O_3 powders. (b) XRD analysis results obtained before and after in situ spark plasma sintering of CNT/amorphous-Al_2O_3 powders. (c) The pulled-out carbon nanotubes on the fracture surface of CNT/alumina nanocomposite when the CNT volume fraction was 1.0%. (d) The agglomerated carbon nanotubes and pores on the fracture surface of CNT/alumina nanocomposite with CNT volume fraction of 1.8%.

the CNT/alumina nanocomposite, fabricated by the molecular level mixing process followed by in situ SPS, shows clear evidence of pulled-out CNTs, which indicates that the CNTs bear significant stress by sharing a portion of the load and, at the same time, toughen the matrix by a bridging effect. Therefore, it is expected that the CNTs within the alumina matrix simultaneously strengthen and toughen the alumina matrix. Furthermore, the chemical bonding between the CNTs and the matrix fabricated by molecular level mixing of CNTs and Al ions can enhance the efficiency of load transfer from matrix to CNTs. However, when the volume fraction of carbon nanotube increases over 1.8 vol.%, the CNTs tend to be agglomerated as shown on the fractured surface in Fig. 2d.

The mechanical properties shown in Fig. 3 strongly support the suggestion of strengthening and toughening by CNTs in the alumina matrix. The hardness of the CNT/alumina composite increases with increasing CNT volume fraction up to about 1%. However, it decreases when the CNT volume fraction increases above about 2% due to the agglomeration of CNTs as shown

in Fig. 2d. The fracture toughness of the CNT/alumina composite increases with increasing volume fraction of CNTs, which is comparable to the results of other researchers [4–7]. It is concluded that the homogeneous distribution of CNTs within the alumina matrix and the formation of strong interfaces between CNTs and alumina enhances both the strength and the toughness of CNT/alumina nanocomposites. It should be noted that multi-walled CNTs were used in the current research. In previous research, it was suggested that only single-walled CNTs could improve the fracture toughness of CNT/alumina nanocomposites [4]. However, the multi-walled CNTs in CNT/alumina nanocomposites, fabricated by the process described above, have improved not only fracture toughness but also hardness in this study. Therefore, the homogeneous distribution of CNTs in the alumina matrix and strong interfacial bonding between CNTs and alumina matrix are the most important factors in obtaining strengthening and toughening of CNT/alumina nanocomposites.

4. Conclusions

The CNT/alumina nanocomposites are fabricated by a molecular level mixing process, followed by an in situ SPS process. The CNT/alumina nanocomposites show homogenously distributed CNTs strongly bonded with the alumina matrix. The CNT/alumina nanocomposites thus fabricated showed an enhanced hardness and toughness compared to monolithic materials, which is based on the load sharing and bridging mechanisms of CNTs in the alumina matrix.
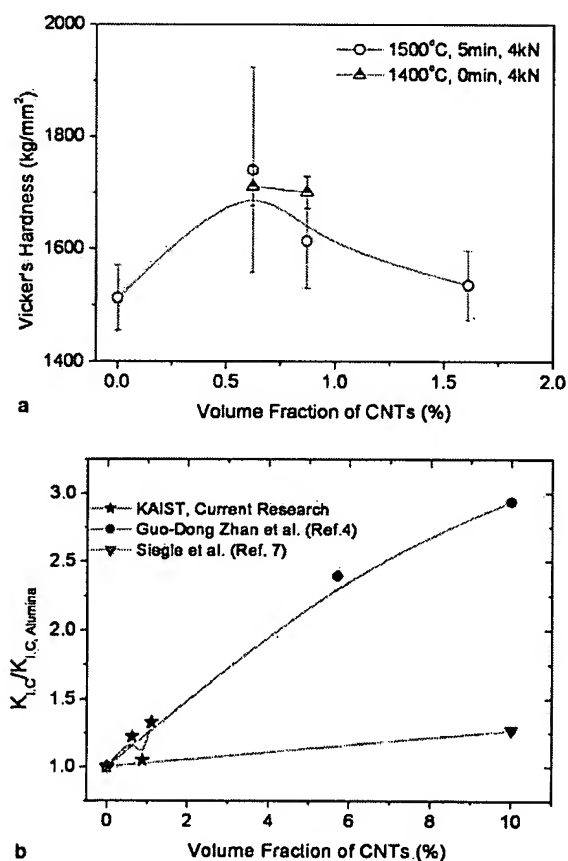
Acknowledgement

Fig. 3. (a) Variation of the hardness of CNT/alumina nanocomposite with varying CNT volume fraction, and (b) variation of the fracture toughness of CNT/alumina nanocomposite, normalized by that of alumina matrix, with increasing volume fraction of CNTs.

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Extraordinary Strengthening Effect of Carbon Nanotubes in Metal-Matrix Nanocomposites Processed by Molecular-Level Mixing**

By *Seung I. Cha, Kyung T. Kim, Salman N. Arshad, Chan B. Mo,* and *Soon H. Hong**

Since the first discovery of carbon nanotubes (CNTs) in 1991, a window to new technological areas has been opened.[1] One of the emerging applications of CNTs is the reinforcement of composite materials to overcome the performance limits of conventional materials.[2,3] Recent developments in CNT/polymer composites have shown the potential for improving the strength of polymers,[2] and this finding has encouraged researchers to use carbon nanotubes as reinforcements for metal and ceramic matrices.[4–7] However, because of the difficulties in distributing CNTs homogeneously in a metal or ceramic matrix by means of traditional composite processes, it has been doubted whether CNTs can really reinforce metals or ceramics.[4–7] Here we report on a CNT-reinforced Cu matrix nanocomposite, fabricated by a novel fabrication process called "molecular-level mixing"; this nanocomposite shows extremely high strength, several times higher than the matrix. The novel process for fabricating CNT/Cu composite powders involves suspending CNTs in a solvent by surface functionalization, mixing Cu ions with the CNT suspension, drying, calcination, and reduction. This process produces CNT/Cu composite powders, whereby the CNTs are homogeneously implanted within the Cu powders. The CNT/Cu nanocomposite, consolidated by spark plasma sintering of CNT/Cu composite powders, is shown to possess three times the strength of the Cu matrix and to have twice the Young's modulus. This extraordinary strengthening effect of carbon nanotubes in metal is higher than that of any other reinforcement ever used for metal-matrix composites.

Several researchers have attempted to fabricate CNT-reinforced metal- or ceramic-matrix composite materials by

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means of traditional powder-metallurgy processes,[4,6,7] which consist of mixing CNTs with matrix powders followed by sintering or hot-pressing. However, these attempts have failed to fabricate CNT/metal or CNT/ceramic composites with homogeneously dispersed CNTs in the matrix. This is mainly due to the strong agglomeration of CNTs in the powder form: the van der Waals' forces between CNTs cause them to mutually attract each other rather than homogeneously disperse. Furthermore, if the CNT/metal or CNT/ceramic nanocomposites are manufactured by conventional processes, most of the CNTs are located on the surfaces of the metal or ceramic powders after mixing.[4,6,7] The conventional process inhibits the diffusion of matrix materials across or along the powder surfaces; hence, sintering cannot proceed without damaging the CNTs or removing them from the powder surfaces. Even if sintering is successful, CNTs are mostly located at grain boundaries of the matrix and are insignificant in improving material performance. At the same time, the most important processing issue is the interfacial strength between the carbon nanotubes and the matrix. In the case of CNT/polymer nanocomposites, the interfacial strength between the CNTs and the polymer matrix is strong because they interact at the molecular level.[2] In the case of CNT/metal or CNT/ceramic nanocomposites, however, the interfacial strength cannot be expected to be high because the CNTs and the matrix are merely blended.[4]

Our strategy for developing a novel fabrication process for CNT/Cu nanocomposites basically involves molecular-level mixing of the reinforcement (CNT) and the matrix material in a solution instead of conventional powder mixing. This new process produces CNT/Cu composite powders, where the CNTs are mainly located within the Cu powders rather than on their surfaces; the chemical bonding between the CNTs and the Cu ions provides a homogeneous distribution of CNTs, as well as high interfacial strength between the CNTs and Cu.

The suggested process for fabricating CNT/Cu composite powders consists of four steps. First, CNT powders produced by thermal chemical vapor deposition are dispersed in a solution such as water or ethanol to make a stable suspension by attaching functional groups onto the CNT surfaces (Figs. 1a,d). There are several chemical methods for attaching functional groups to CNT surfaces.[8–11] Once the functional groups are attached to the CNTs, the electrostatic repulsive
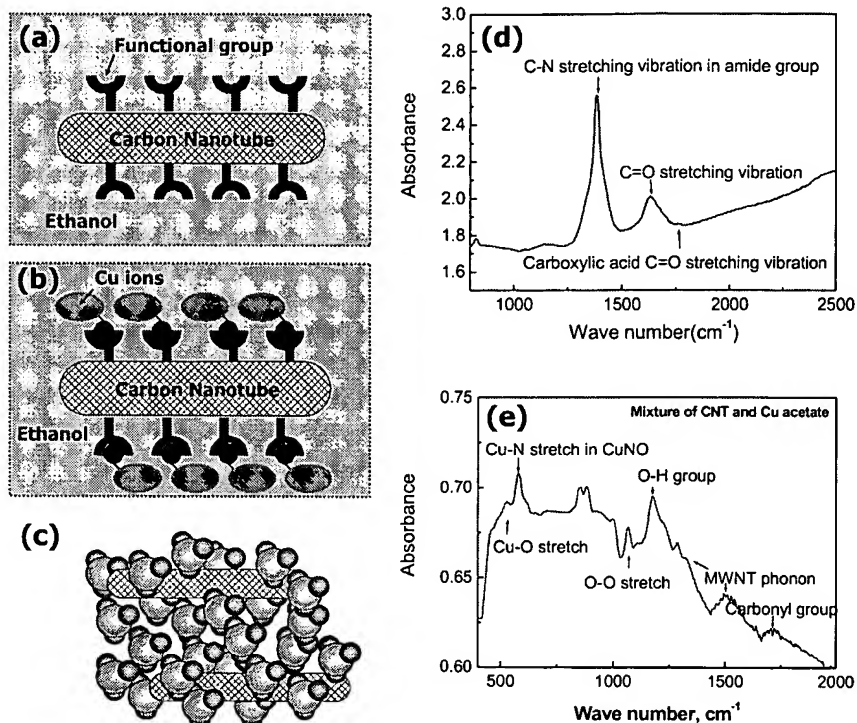

Figure 1. Schematics depicting strategies and procedures for the molecular-level mixing process to fabricate CNT/Cu composite powders: a) making a functionalized stable CNT suspension in ethanol, b) dissolution of a Cu salt such as $Cu(CH_3COO)_2$ and attaching Cu ions to the functional groups on the surface of the CNT, c) vaporization of the solvent by heating. d) Fourier-transform IR (FTIR) spectroscopic analysis of CNTs after purification, which shows that some functional groups containing N and O formed on the surface of the CNTs, and e) FTIR analysis of dried powders before calcination, which shows that Cu ions reacted with the functional groups on the CNTs. (MWNT: multiwalled nanotube.)

force between the CNTs overcomes the van der Waals' force to form a stable suspension within the solvent. Second, a salt containing Cu ions—copper acetate in the current study—is dissolved in the CNT suspension. The solution now consists of suspended CNTs, solvent, ligands, and metal ions. Additional sonication treatment assists the dispersion of Cu ions among the suspended CNTs and promotes the reaction between the Cu ions and the functional groups on CNT surfaces (Figs. 1b,e). The third step is to dry the solution by heating at 100–250 °C in air. During this process, the solvent and ligands are removed and the Cu ions on the CNTs are oxidized to form powders (Fig. 1c). The fourth and final step is the calcination and reduction process to obtain chemically stable crystalline powders. The powders obtained in the third step are generally a mixture of CuO and Cu_2O. These powders are changed into stable CNT/CuO by heating at 300 °C in air and are then reduced to CNT/Cu composite powders by a reduction process under a hydrogen atmosphere.

The above four-step process gave homogeneously dispersed CNTs within Cu powders, as shown in Figure 2. The most important feature of this process is that CNTs and Cu ions are mixed with each other at the molecular level. That is, the
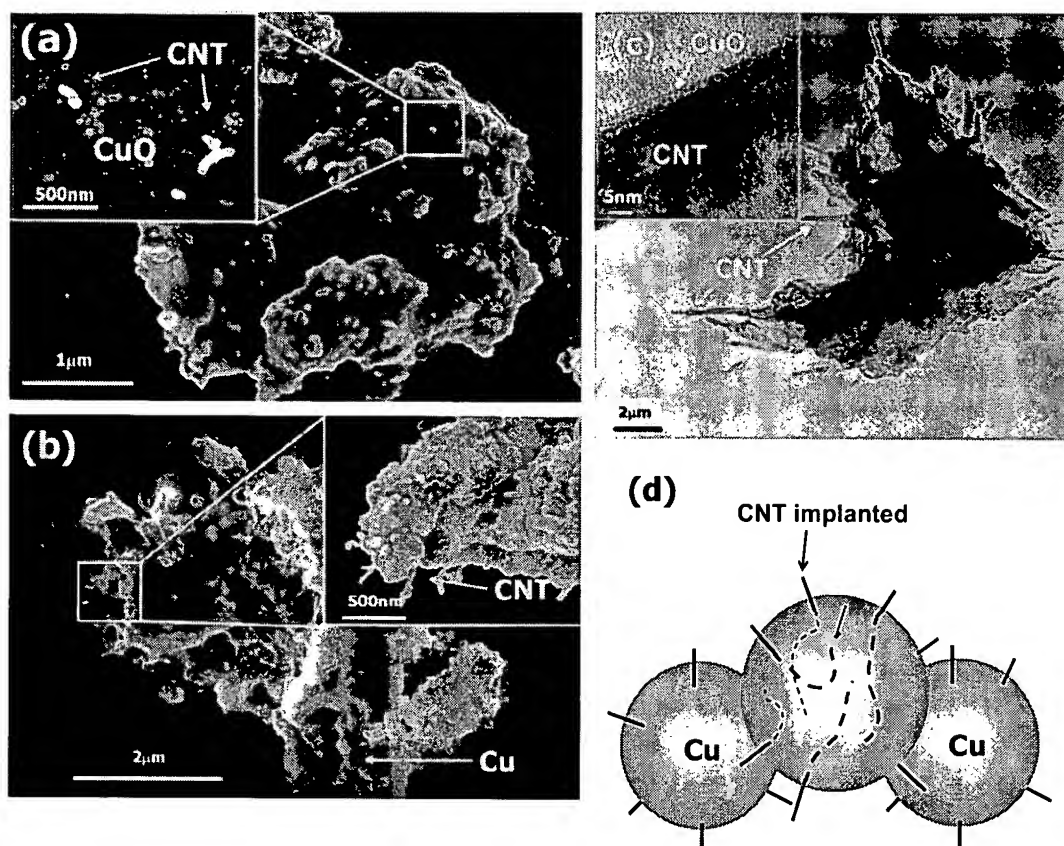
Figure 2. Microstructures of CNT/CuO and CNT/Cu composite powders, where the CNTs are homogeneously implanted in the matrix. a) Scanning electron microscopy (SEM) micrographs of CNT/CuO composite powders, b) SEM micrographs of CNT/Cu composite powders, c) transmission electron microscopy (TEM) micrographs of CNT/CuO composite powders, showing that CNTs are implanted within the matrix with good bonding at the interface between CuO and the CNTs (inset), and d) schematic depiction of the CNT/Cu composite powder.

CNTs are located within the powders rather than on the powder surfaces. The morphologies of the CNT/CuO and CNT/Cu powders show an ideal composite microstructure, which displays spherical morphologies with CNTs implanted in the powders (Figs. 2a,b). The implanted CNTs in the CNT/Cu composite powders could be seen more clearly using transmission electron microscopy (TEM, Fig. 2c). The finally obtained CNT/Cu composite powder, wherein CNTs are implanted in the Cu matrix, is schematically depicted in Figure 2d.

The CNT/Cu composite powders fabricated by the molecular-level mixing process were consolidated into a bulk CNT/Cu nanocomposite with full densification by spark plasma sintering, which can produce a high heating rate of 100 °C min^{-1} and rapid consolidation through high-joule heating and a spark plasma generated between the powders. A schematic depiction of the spark plasma sintering process and the microstructure of the resulting CNT/Cu nanocomposites is shown in Figure 3a. The consolidated CNT/Cu nanocomposite shows a homogeneous distribution of carbon nanotubes within the Cu matrix, which had not been obtained until now for CNT/metal or CNT/ceramic nanocomposites (Fig. 3b). Particularly, the

TEM micrograph (Fig. 3c) shows that the carbon nanotubes form a network within the Cu grains. Moreover, the Cu grains show a very low dislocation density when they are reinforced by carbon nanotubes.

The mechanical properties of the CNT/Cu nanocomposite were characterized using compressive tests. As shown in Figure 4a, the compressive yield strengths of CNT/Cu nanocomposites were much higher than that of the Cu matrix, which was fabricated by the same process without adding CNTs. A 5 vol.-% CNT-reinforced Cu matrix nanocomposite showed a yield strength of 360 MPa, which is 2.3 times higher than that of Cu. In the case of 10 vol.-% CNT-reinforced Cu, the yield strength was 455 MPa, which is more than 3 times higher than that of Cu. Moreover, the Young's modulus of the CNT/Cu nanocomposite increased as the volume fraction of carbon nanotubes was increased, as shown in Figure 4b.

Such remarkable strengthening by CNT reinforcement was due to the high load-transfer efficiency of CNTs in the metal matrix. High load-transfer efficiency was caused by strong interfacial strength between CNTs and Cu, which originated from chemical bonds formed during the molecular-level mix-

(a)

Spark Plasma Sintering Process

Pressure   Pulsed Current

CNT/Cu Composite Powders

Mold

Punch

Schematic microstructure of CNT/Cu nanocomposite

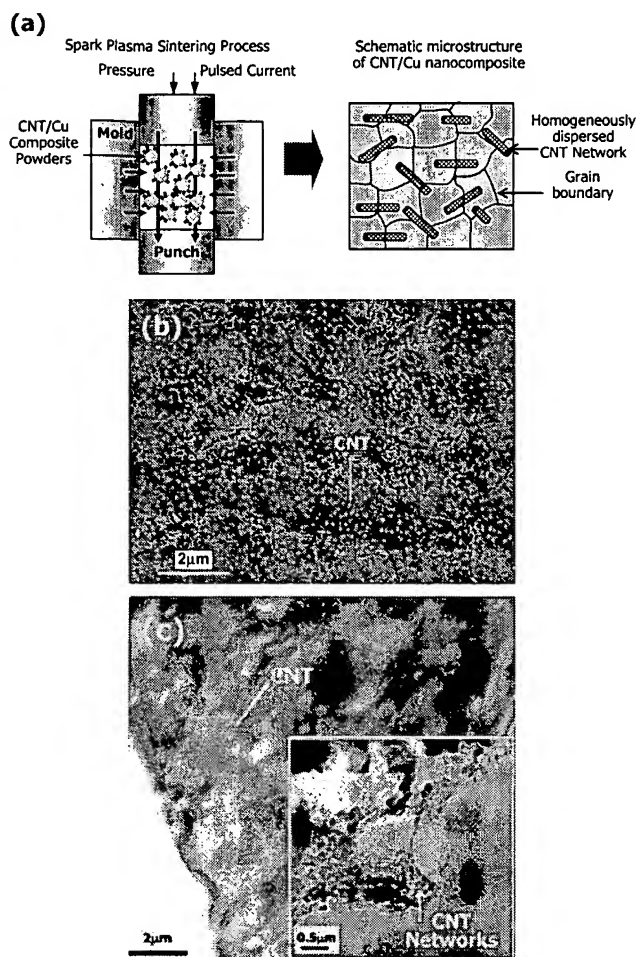Homogeneously dispersed CNT Network

Grain boundary

Figure 3. a) Schematic of the spark plasma sintering process and the resulting microstructure of the CNT/Cu nanocomposite. b) SEM micrographs showing homogeneous distribution of CNTs in the CNT/Cu nanocomposite with 5 vol.-% of CNTs, as revealed after chemical etching. c) TEM micrographs showing a three-dimensional network of CNTs in the Cu grains.

ing process. The yield strength of the metal-matrix composites can be expressed as

$$\sigma = \sigma_m(1 + V_f R) \tag{1}$$

where R is the strengthening efficiency of reinforcement, V_f is the volume fraction of reinforcement, and σ_m is the yield strength of the matrix.[12] Using the generalized shear-lag model, the strengthening efficiency R can be expressed as $S/2$, where S is the aspect ratio of reinforcement, i.e., the ratio between the diameter and length of reinforcement.[12] Using this theory, the calculated yield strengths of 5 vol.-% and 10 vol.-% CNT reinforced Cu matrix composites are 370 MPa and 589 MPa, respectively. These values are higher than those measured by the compressive test. This disparity is derived mainly from the misalignment of the carbon nanotubes within the Cu matrix.[12] The above equation is based on the perfect
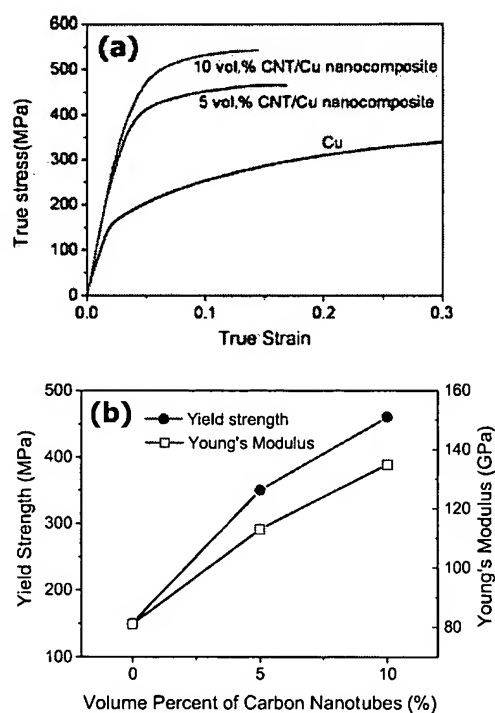

Figure 4. Mechanical properties of CNT/Cu nanocomposites: a) stress–strain curves of CNT/Cu nanocomposites obtained by compressive testing, and b) yield strength and Young's modulus of CNT/Cu nanocomposites with increasing volume percentage of CNTs.

alignment of fibrous reinforcement in the loading direction. In the CNT/Cu nanocomposite, however, the carbon nanotubes form a three-dimensional network within the Cu matrix, and as a result the load-transfer efficiency decreases. It must be noted that strengthening by reinforcement is separate from other strengthening mechanisms, including precipitation strengthening, grain-refinement strengthening, and work hardening. Therefore, if the strength of the Cu matrix reaches 1 GPa using other strengthening mechanisms, such as nanostructuring of grain size, the strength of the CNT/Cu nanocomposite can be enhanced over 3 GPa by strengthening of the CNTs. Nonetheless, the strengthening effect of CNT reinforcement is the greatest of all reinforcements used for metal matrix composites. As shown in Table 1, the reinforcement efficiency, i.e., the strengthening effect of a given volume percentage of reinforcement on the matrix, is almost eight times higher for carbon nanotubes than for SiC particles and three times higher than for SiC whiskers, which are the two most widely used strengthening reinforcements for metal matrices. This indicates that carbon nanotubes are confirmed to be the most effective reinforcements.

Lastly, it is worth mentioning here that the molecular-level mixing process described above can also be applied to CNT/ceramic nanocomposites by omitting the reduction step. As shown in the Supporting Information, CNT/alumina nanocomposites can be fabricated by using $Al(NO_3)_3 \cdot 9H_2O$. Here, as in the case of the CNT/Cu nanocomposite, CNTs were

Table 1. Strengthening efficiencies of several reinforcement materials. The strengthening efficiency of reinforcement R is defined as the ratio of the amount of yield strength increase of the composite to that of the matrix by the addition of reinforcement materials [13–18].

Reinforcement		Matrix		Composite	Strengthening efficiency
Type	Vol. [%]	Type	Yield strength σ_m [MPa]	Yield strength σ_c [MPa]	of reinforcement R [a]
Alumina Particle	10	Zn/Al/Cu	310	380	2.3
Alumina Fiber	10	Al/12Si/Ni/Cu	210	247	1.7
SiC Particle	10	Al alloy CW67	340	425	2.5
SiC Whisker	10	Al alloy AZ91	87	154	7.6
Carbon Fiber	10	Al alloy A357	360 [b]	499 [b]	3.9
Carbon Fiber	10	Cu	232 [b]	347 [b]	5.0
Carbon Nanotube	10	Cu	150	455	20.3

[a] Strengthening efficiency of reinforcement $R = (\sigma_c - \sigma_m)/V_f \sigma_m$.

[b] The strength of the carbon-fiber-reinforced composite is fracture stress.

implanted within the alumina matrix, and the CNT/alumina nanocomposite showed much-improved strength and fracture toughness.

In summary, CNT/Cu nanocomposites with homogeneously dispersed CNTs within the Cu matrix can be fabricated by means of a molecular-level mixing process, which consists of mixing Cu ions with functionalized CNTs in a solvent. The yield strength of the CNT/Cu nanocomposite was shown to be three times higher than that of Cu alone. Carbon nanotubes showed the most effective strengthening efficiencies among all reinforcement materials: eight times higher than SiC particles and three times higher than SiC whiskers.

Experimental

Fabrication of CNT/Cu Composite Powders: Multiwalled carbon nanotubes, with diameters of 10–40 nm and fabricated by thermal chemical vapor deposition, were purified and functionalized by acid treatment using HF, H_2SO_4, and HNO_3. The CNTs were stirred for 24 h in HF and then cleansed with a mixed solution of H_2SO_4/HNO_3 in a 3:1 ratio. 20 mg of the purified CNTs was dispersed in 500 mL ethanol by sonication for 2 h to form a stable suspension. 3 g of $Cu(CH_3COO)_2·H_2O$ (Aldrich) was added to the CNT suspension, which was sonicated again for 2 h. The solution was vaporized with magnetic stirring at 100 °C, and the dried powders were calcinated at 300 °C in air. The calcinated powders were reduced at 250 °C for 3 h under a hydrogen atmosphere. The average number of walls in the multiwalled carbon nanotubes was measured to be 20 by TEM observations. The density of multiwalled carbon nanotubes with an average diameter of 40 nm and average length of 2 μm was calculated to be 1.8 g cm^{-3}. The weight percent of CNTs was 1.0 for the 5 vol.-% CNT/Cu nanocomposite and 2.2 for the 10 vol.-% CNT/Cu nanocomposite.

Consolidation of CNT/Cu Composite Powders: The CNT/Cu composite powders were pre-compacted in a graphite mold, 15 mm in diameter, under a pressure of 10 MPa. The pre-compacted powders were consolidated by spark plasma sintering at 550 °C for 1 min in a vacuum of 0.1 Pa with an applied pressure of 50 MPa. The heating rate up to the sintering temperature was maintained at 100 °C min^{-1}. The final size of the spark plasma sintered CNT/Cu nanocomposite was 15 mm in diameter and 5 mm in thickness.

Characterization: Microstructure characterization of the CNT/Cu composite powders and nanocomposites were carried out using optical microscopy, high-resolution scanning electron microscopy (HRSEM), and TEM. The volume fraction of CNTs was determined by analyzing the carbon contents using an elemental analyzer (Fi-

sons EA1110) and a C/S analyzer (ELTRA CS800). Compressive tests were performed using an Instron 5583 with a crosshead speed of 0.2 mm min^{-1}. The sample had a cylindrical disc shape, and was 2 mm in height and 1.5 mm in diameter.

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